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Steric control in the metal-ligand electron transfer of iminopyridine-ytterbocene complexes

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Abstract

© 2018 The Royal Society of Chemistry. A systematic study of reactions between Cp∗2Yb(THF) (Cp∗ = η5-C5Me5, 1) and iminopyridine ligands (IPy = 2,6-iPr2C6H3NCH(C5H3N-R), R = H (2a), 6-C4H3O (2b), 6-C4H3S (2c), 6-C6H5 (2d)) featuring similar electron accepting properties but variable denticity and steric demand, has provided a new example of steric control on the redox chemistry of ytterbocenes. The reaction of the unsubstituted IPy 2a with 1, either in THF or toluene, gives rise to the paramagnetic species Cp∗2YbIII(IPy)- (3a) as a result of a formal one-electron oxidation of the YbII ion along with IPy reduction to a radical-anionic state. The reactions of 1 with substituted iminopyridines 2b-d, bearing aryl or hetero-aryl dangling arms on the 6 position of the pyridine ring occur in a non-coordinating solvent (toluene) only and afford coordination compounds of a formally divalent ytterbium ion, coordinated by neutral IPy ligands Cp∗2YbII(IPy)0 (3b-d). The X-ray diffraction studies revealed that 2a-c act as bidentate ligands; while the radical-anionic IPy in 3a chelates the YbIII ion with both nitrogens, neutral IPy ligands in 3b and 3c participate in the metal coordination sphere through the pyridine nitrogen and O or S atoms from the furan or thiophene moieties, respectively. Finally, in complex 3d the neutral IPy ligand formally adopts a monodentate coordination mode. However, an agostic interaction between the YbII ion and an ortho C-H bond of the phenyl ring has been detected. Imino-nitrogens in 3b-d are not involved in the metal coordination. Variable temperature magnetic measurements on 3a are consistent with a multiconfigurational ground state of the Yb ion and suggest that the largest contribution arises from the 4f13-radical configuration. For complexes 3b and 3c the data of magnetic measurements are indicative of a YbII-closed shell ligand electronic distribution. Complex 3d is characterized by a complex magnetic behavior which does not allow for an unambiguous estimation of its electronic structure. The results are rationalized using DFT and CSSCF calculations. Unlike diazabutadiene analogues, 3a does not undergo a solvent mediated metal-ligand electron transfer and remains paramagnetic in THF solution. On the other hand, complexes 3b-d readily react with THF to afford 1 and free IPy 2b-d.

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